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Title: **"Differences in anthocyanins extractability from grapes to wines according to variety"**

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To clarify why highly-colored grapes do not always produce highly-colored wines, the authors compared the anthocyanin extractability of different Spanish varieties, hoping it would help determine optimal fermentation conditions for each wine style desired.

• Anthocyanins are located in the skins of red varieties within a cell compartment called a vacuole. Extraction requires that the thick cell walls be degraded, and the thin vacuole membranes broken for the contents to diffuse into the wine. This wall/membrane degradation is maximized when the pH is very low (pH 1.0). But the wall maceration during winemaking conditions tends to take place at pH values closer to 3.6. Anthocyanin extractability –measured with the *extractability index*- is considered optimal when amounts extracted at winemaking conditions (pH 3.6) approach those extracted during total cell disruption (pH 1.0), that is, when the difference between both is *small*. That's why, throughout this text, "low extractability index" means "high extractability in the winery". Let's not let that confuse us! We would prefer varieties with a *low* extractability index.

$$\text{Extractability index} = \frac{\text{Anthocyanins extracted at pH 1.0} - \text{Anthocyanins extracted at pH 3.6}}{\text{Anthocyanins extracted at pH 1.0}} \times 100$$

• This study takes place in southeastern Spain (D.O. Jumilla) in 2003, targeting the following varieties: Cabernet Sauvignon, Merlot, Syrah, and Mourvedre (also known as Monastrell or Mataro). Because Mourvedre is the most important variety in the Jumilla appellation, the authors also compare Mourvedre grapes from two different locations (Mourvedre A and Mourvedre B). Wines were made in triplicate for each of the varieties.

• For each variety and corresponding wine, the authors measured the following 7 parameters:
1) Grape anthocyanins (HPLC)**.** When the results are expressed as concentration (µg/g of skin), **Mourvedre A and Syrah had the highest concentration of anthocyanins**. Mourvedre was found to have the largest berries among the varieties compared, and Syrah and Merlot, the smallest berries. Even when the results were expressed as content (mg/kg of berries), Mourvedre A and Syrah still had the highest values.

• **2) Extractability index.** Mourvedre was the variety with the highest extractability index (hardest color to extract). Syrah, Cabernet Sauvignon and Merlot all had similar, lower extractability indices (easier to extract). The authors discuss whether the slightly lower Brix of Mourvedre at harvest, compared to the other varieties, might have impacted these results. They don't think so. When they allowed the sugars to increase from 24.4 to 26.2 Brix, Mourvedre extractability index did not change.

• **3) Skin and seed tannins (**Harbertson and Adams method)**. Mourvedre A and Cabernet Sauvignon had the highest levels of *skin tannins*** (both as concentration and as content . As for *seed tannins*, Cabernet Sauvignon and Merlot had the highest concentration of seed tannins. When express as a per berry basis, there were no important differences in seed tannins among varieties.

• **4) Wine anthocyanins** (HPLC)**.** Total amount of anthocyanins was significantly higher in Mourvedre A, Cabernet Sauvignon, and Syrah.

• **5) Wine color.** The authors checked whether the extractability indices found in this study correlated with the chromatic characteristics of the wines. The short answer is no. Mourvedre A, Syrah and Cabernet Sauvignon wines all presented similar color values (A420 + A520 + A620), even if the anthocyanins concentrations found in the grapes were different. Total phenols (A280) were higher in Cabernet Sauvignon, Syrah, and Merlot wines, indicating that more phenolic compounds had been extracted for these varieties. Merlot wines had an unusual behavior in that they had a high hue and a high yellow percentage. The authors point out that Merlot, with a low anthocyanin and a high tannin concentrations, might be an example of a variety with an unbalanced anthocyanin/tannin ratio.

• **6) Copigmented anthocyanins** (Levengood and Boulton method)**.** Copigmentation percentages were very similar for most of the varieties. Therefore, authors point out that differences in observed color are likely due to polymers of anthocyanins.

• **7) Macerated skin anthocyanins.** The authors studied the anthocyanins remaining in the crushed skins after maceration to seek confirmation of the respective extractability indices. The crushed skins from Mourvedre (both A and B) showed the greatest concentration of anthocyanins, about 15-20% of the initial grape values (which is in agreement with the lowest extractability into the wine). The remaining varieties all showed lower levels of anthocyanins remaining in the crushed skins (less than 12%).

• **Correlations.** The authors found the total phenols in grapes (at the maceration pH 3.6) to be highly correlated with the total phenols in the wines, as well as with total wine tannin. The extractability index also correlated best with the amount of total phenols in the wine. As for tannins, the authors did not find any good correlation between skin tannin and any of the wine parameters, but yes between seed tannin and wine tannin. The authors note that the lack of correlation between tannins in grapes and tannins in the corresponding wines in a previous study might have been due to the lack of standardization of the winemaking conditions. In the current study, in which winemaking practices were the same for all wines, grape seed tannin concentration was highly correlated with wine tannin concentration.

In conclusion, wine color intensity did not correlate with the total anthocyanins observed in grapes (measured intact with HPLC or at pH 1.0), but it did correlate with the anthocyanins extracted at wine maceration conditions (pH 3.6). The authors conclude that the key chromatic parameters a wine will have could best be predicted by measuring the following three phenolic parameters: 1) anthocyanins at pH 3.6, 2) total phenols at pH 3.6, and 3) seed tannin content. Knowledge of this "phenolic potential" at time of harvest would, in turn, allow for the optimal fermentation parameters to be planned. The authors leave us with some examples based on the extractability indices they obtained for each variety:

- *Mourvedre*, with the highest extractability index, would require long maceration periods, and frequent pump-overs.
- *Merlot*, with low anthocyanins concentration and high tannin concentration, but low extractability index, would benefit most from short maceration periods (an excess extraction of tannins would increase the amount of yellow color and the astringency).

- *Syrah* could be favored with frequent pump-overs for increasing tannin concentration, especially if the wine is destined to age.
- *Cabernet Sauvignon*, with high extractability index and high tannin concentration, would be expected to give good results with both short (young wines) and long macerations (wines destined to age).

		Highest in:	Lowest in:
Berry	**Size**	Mourvedre A > Mourvedre B > Syrah [1]	C. Sauvignon = Merlot
	Anthocyanin concentration	Mourvedre A > Syrah > Mourvedre B	Merlot > C. Sauvignon [2]
	Extractability index	Mourvedre A = Mourvedre B	Merlot = C.Sauvignon = Syrah
	Skin tannin content	Mourvedre A = Mourvedre B	Merlot = Syrah > C. Sauvignon
	Seed tannin content	Mourvedre A = Mourvedre B	Syrah > C. Sauvignon = Merlot
Wine	**Anthocyanin concentration**	Mourvedre A = C. Sauvignon = Syrah	Merlot > Mourvedre B
	Color intensity [3]	Syrah = Mourvedre A = C. Sauvignon	Mourvedre B = Merlot
	Copigmented color [3]	Syrah > C. Sauvignon = Merlot = Mourvedre B	Mourvedre A
Pomace	**Anthocyanin concentration**	Mourvedre A > Mourvedre B	Merlot > C. Sauvignon = Syrah

[1] ">/<" and "=" indicate significant differences or lack thereof ($p<0.05$)
[2] 'A>B' under the "Lowest in:" column means than A is significantly **lower** than B
[3] Table represents values taken after ML fermentation

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